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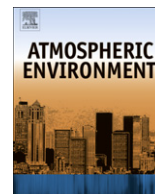
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Abundances and variability of tropospheric volatile organic compounds at the South Pole and other Antarctic locations

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ABSTRACT

Multiyear (2000–2006) seasonal measurements of carbon monoxide, hydrocarbons, halogenated species, dimethyl sulfide, carbonyl sulfide and C₁–C₄ alkyl nitrates at the South Pole are presented for the first time. At the South Pole, short-lived species (such as the alkenes) typically were not observed above their limits of detection because of long transit times from source regions. Peak mixing ratios of the longer lived species with anthropogenic sources were measured in late winter (August and September) with decreasing mixing ratios throughout the spring. In comparison, compounds with a strong oceanic source, such as bromoform and methyl iodide, had peak mixing ratios earlier in the winter (June and July) because of decreased oceanic production during the winter months. Dimethyl sulfide (DMS), which is also oceanically emitted but has a short lifetime, was rarely measured above 5 pptv. This is in contrast to high DMS mixing ratios at coastal locations and shows the importance of photochemical removal during transport to the pole. Alkyl nitrate mixing ratios peaked during April and then decreased throughout the winter. The dominant source of the alkyl nitrates in the region is believed to be oceanic emissions rather than photochemical production due to low alkane levels.

Sampling of other tropospheric environments via a Twin Otter aircraft included the west coast of the Ross Sea and large stretches of the Antarctic Plateau. In the coastal atmosphere, a vertical gradient was found with the highest mixing ratios of marine emitted compounds at low altitudes. Conversely, for anthropogenically produced species the highest mixing ratios were measured at the highest altitudes, suggesting long-range transport to the continent. Flights flown through the plume of Mount Erebus, an active volcano, revealed that both carbon monoxide and carbonyl sulfide are emitted with an OCS/CO molar ratio of 3.3×10^{-3} consistent with direct observations by other investigators within the crater rim.

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1. Introduction

Atmospheric research in Antarctica has been limited due to its remote location. However despite this constraint, unique atmospheric phenomena have been observed. The first of these was the formation of a hole in the ozone layer over Antarctica each spring (Farman et al., 1985). Subsequent research documented other findings including the emission of nitrogen oxides (NO_x) from sunlit snowpacks (Jones et al., 2000, 2001; Davis et al., 2001, 2004, 2008; Oncley et al., 2004; Helmig et al., 2008a), emission of

formaldehyde (Hutterli et al., 2002, 2004), near surface net ozone formation on the plateau (Crawford et al., 2001; Chen et al., 2004; Helmig et al., 2008b; Legrand et al., 2009), and elevated hydroxyl radical concentrations above the snowpack (Mauldin et al., 2001, 2004, 2010).

Despite this increase in Antarctic research, there have been relatively few investigations of the seasonal distribution of volatile organic compounds (VOCs) in this region. This is most apparent at the South Pole where measurements of hydrocarbon compounds have been limited to samples collected primarily during the austral summer (Khalil and Rasmussen, 1986) and measurement of VOCs with oceanic sources sampled over a period of 1 year (Swanson et al., 2004). The current study is a continuation of the South Pole measurements by Swanson et al. (2004) and includes measurements of carbon monoxide (CO), methane (CH₄), non-methane

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hydrocarbons (NMHCs), halogenated species, dimethyl sulfide (DMS), carbonyl sulfide (OCS) and short-chain alkyl nitrates. In addition, airborne measurements are reported for the austral summer of 2005. These provide a comparison between the coastal and continental interior of Antarctica and the first altitudinal profiles for many species sampled in the Antarctic troposphere.

The South Pole is far removed from virtually all anthropogenic sources of VOCs with the nearest populated regions being the southern areas of Australia, New Zealand and South America. Thus, transport from these regions can only be a source of relatively long-lived species. By contrast, transport from the Southern Ocean can serve as a significant source of VOCs. These compounds are produced by algae and plankton in the ocean and are subsequently released into the atmosphere. Species with reported oceanic sources include methyl halides (Laturnus et al., 1998), bromoform (CHBr_3) (Quack and Wallace, 2003), DMS (Lovelock et al., 1972; Todd et al., 2007) and alkyl nitrates (Atlas et al., 1993). In particular, emissions from the Southern Ocean have been shown to have a large influence on atmospheric levels of DMS measured at several coastal sites at levels of over 100 pptv (e.g., Berresheim et al., 1998; Jourdain and Legrand, 2001; Legrand et al., 2001; Preunkert et al., 2007 and references therein).

In addition to reporting seasonal VOC trends in Antarctica, the measurements reported here allow for a comparison with earlier measurements in Antarctica as well as at the Arctic research station at Summit, Greenland. Seasonal measurements of VOCs at Summit ($72^\circ 34' \text{ N}$, $38^\circ 29' \text{ W}$, 3200 m altitude) date back to 1997 and are discussed in Swanson et al. (2003) and in greater detail in Beyersdorf (2007). Both Summit and the South Pole represent high altitude, non-coastal sites. However, Summit is located at a significantly lower latitude than the South Pole and is in much closer proximity to anthropogenic sources due to its location in the northern hemisphere. In addition, upslope flow from marine areas can frequently reach the Summit site; whereas, this meteorological condition occurs infrequently at the South Pole.

2. Sampling

Sampling at the South Pole was carried out in conjunction with the Investigation of Sulfur Chemistry in the Antarctic Troposphere (ISCAT) and the ANtarctic Tropospheric Chemistry Investigation (ANTCI) programs during two different time periods: November 2000–October 2001 and November 2003–November 2006. Most samples were collected during the austral spring and summer (October–March) with a lower and more variable sampling frequency during the winter. For example, weekly sampling occurred during the winters of 2004 and 2006 while only four samples were collected during the winter of 2001 and five during the winter of 2005. This sporadic sampling was the result of logistical problems involving the shipping of canisters from Antarctica during the winter.

At the South Pole, sampling was carried out at the Atmospheric Research Observatory (ARO) building located at the Amundsen–Scott Research Station. The inlet of the stainless steel sampling line was located at the top of a tower on the roof of the ARO building, placing it approximately 16 m above the snow's surface. Usually sampling was only performed when the wind direction was contained within the “clean air sector,” an area that typically is not influenced by pollution from the research station's runway and power generator (Davis et al., 2004). A metal bellows pump (Senior Aerospace, Moorpark, CA) was used in order to pressurize whole air samples to 30 psi (207 kPa).

As previously noted, samples were also collected during the ANTCI 2005 airborne study (Slusher et al., 2010). The aircraft used was a de Havilland DHC-6 Twin Otter. The VOC sampling inlet was

located in front of the prop-line with stainless steel tubing conducting air flow to a metal bellows pump located in the cabin. Sample canisters were housed in the rear compartment of the plane. A total of 12 research flights were flown during November and December 2005. Nine of these flights were based out of McMurdo Research Station with one out of the South Pole and two transit flights between McMurdo and the South Pole.

Samples were collected in electropolished 2-L stainless steel canisters. Prior to shipment, the canisters were conditioned and evacuated. Following this, 10 torr (1.3 kPa) of purified water was added to each canister to passivate active surface sites. Previous studies using these canisters have shown that the addition of water and pressurizing the samples leads to improved analyte stability in the canisters (Simpson et al., 2001). Specifically, DMS was found to show no decay when stored in the canisters for up to four months (Swanson et al., 2004). In addition, atmospheric oxidants (such as hydroxyl radical and ozone) are removed quickly by reaction with the canister surface causing no degradation in compounds with high ozone reaction rates (such as alkenes) (Sive, 1998).

3. Analytical methods

Upon completion of each of the field studies, canister samples were returned to the University of California, Irvine for analysis. Typically, these samples were analyzed within 3 months of their collection. However, because of a lack of air travel from the South Pole, samples collected during the winter were frequently not analyzed for up to 6 months after collection.

Analysis of samples for carbon monoxide, hydrocarbons, halogenated compounds, sulfur species and alkyl nitrates involved three different gas chromatographic (GC) systems. The first used a flame ionization detector (FID) for determining the levels of methane (Blake and Rowland, 1986). On a second system, CO was first separated from other species by GC and then converted to methane where it was detected by an FID sensor.

Non-methane hydrocarbons, halocarbons, sulfur species and alkyl nitrates were measured via a three GC system which is described in detail by Colman et al. (2001). In brief, an aliquot of each sample was pre-concentrated in a stainless steel loop containing glass beads cooled with liquid nitrogen. The loop was then heated to re-volatilize the sample, flushed by a helium carrier and split into five different flows output to five different column–detector combinations. The NMHCs were detected by two FIDs while halocarbons were measured by two electron capture detectors (ECDs). A quadrupole mass selective detector (MSD) was used for quantification of DMS and OCS and provided a second method for the detection of the other VOCs.

Quantification of the compounds was performed by the analysis of whole air standards after every eight samples. The limit of detection (LOD) was 3 pptv for all hydrocarbons and 1 pptv for DMS and OCS. The compounds measured by the ECDs had lower LODs (0.1 pptv for bromoform and 0.01 pptv for methyl iodide and the alkyl nitrates). Analyses of the Summit, Greenland samples were made using the same analytical system and whole air standards. The analytical accuracy of the system ranges from 2 to 20% (Blake et al., 2001). The whole air standards and analytical results are regularly compared with other laboratories including participation in the Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE) (Apel et al., 2003). In addition, samples have been collected during numerous field campaigns and compared to in situ analyte sampling. For example, during the 1999 aircraft-based NASA Pacific Exploratory Mission-Tropics B (PEM-Tropics B) canister DMS measurements agreed well with in-flight analysis employing GC/MSD with intercomparison slopes of 0.986 for all samples and 0.966 at DMS mixing ratios below 50 pptv (Simpson

et al., 2001). Measurement precision also varied based on the compound measured (Blake et al., 2001). The precision was 1% or 1.5 pptv (whichever is larger) for alkanes and alkynes and 3% or 3 pptv for the alkenes. For halocarbons, precisions ranged between 0.01 pptv for methyl iodide and 1 pptv for methyl chloride. Previous campaigns have also determined a DMS precision of 15% or 1 pptv (whichever is larger) at mixing ratios below 10 pptv.

4. Results and discussion

4.1. South Pole carbon monoxide and hydrocarbons

The primary sink of atmospheric CO and hydrocarbons is reaction with the hydroxyl radical (OH). Because photolysis is the primary source of OH, its maximum concentrations occur during the summer months. Thus air masses arriving at the South Pole during the summer have had higher OH exposure (more removal of VOCs) during transport than those during the winter. This results in a seasonal cycle for CO and the NMHCs in which a maximum in concentration is seen during the austral winter and a minimum in the summer (shown for ethane in 2004 in Fig. 1). To a first approximation, this seasonal cycle can be represented by a sinusoidal curve. However, the long winter period with no photolytic activity, caused the profiles to deviate from a sinusoidal fit. Thus, for our analysis a Fourier series fit (1–5 harmonics with a periodicity of 365 days) has been used to approximate the seasonal cycle of the VOCs for the two sampling time-periods that involved full year data collection, e.g., January 1, 2004–December 31, 2004 (hereafter referred to as “2004”) and November 23, 2005–November 22, 2006 (“2006”). In addition, an “average year” has been defined by fitting all of the data to a similar Fourier series.

The seasonal data for CO and hydrocarbons, using the Fourier series fits, are listed in Table 1. The annually averaged CO did not significantly vary between 2004 and 2006 with an average mixing ratio of 60 ± 9 ppbv for the entire period. Regarding the NMHCs, only long-lived species (lifetimes longer than 10 days with respect to reaction with OH) with significant emissions were observed year-round at mixing ratios above 3 pptv (i.e. ethane, ethyne, propane, *n*-butane and benzene). In contrast, ethene (OH lifetime of 1–2 days) is only observed above its LOD during the winter months. Likewise, *i*-butane (which is long-lived but has lower anthropogenic emissions) is only measured during the winter. No other NMHCs were routinely measured above their LOD. This is in comparison to measurements in the Arctic (Summit, Greenland) where short-lived species including ethene are observed

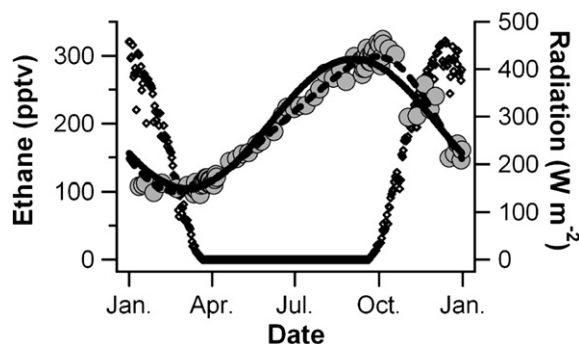


Fig. 1. Ethane measured at the South Pole during 2004 (circles) with a sinusoidal fit (solid line) and a Fourier series fit (dashed line). Average daily solar radiation (300–2800 nm) measured at the South Pole in 2004 is shown by the open diamonds (ESRL, 2007). This is used as a proxy for the photolytic activity the air mass experiences during transport to the South Pole.

Table 1

Interannual variation of CO and hydrocarbons during year-round sampling periods at the South Pole^a.

Compound	Year	Average ^b	Minimum ^c	Maximum ^c	Ratio ^d
CO (ppbv)	2004	61 (11)	44 (Feb 10)	77 (Oct 5)	1.8
	2006	59 (7)	49 (Feb 19)	70 (Sep 15)	1.4
	Average year	60 (9)	45 (Jan 30)	72 (Sep 21)	1.6
Methane (ppmv)	2004	1.731 (0.011)	1.717 (Mar 5)	1.748 (Aug 26)	1.02
	2006	1.724 (0.011)	1.709 (Mar 3)	1.739 (Sep 2)	1.02
	Average year	1.725 (0.011)	1.706 (Feb 16)	1.738 (Sep 9)	1.02
Ethane	2004	196 (69)	100 (Feb 23)	299 (Sep 28)	3.0
	2006	205 (64)	119 (Feb 13)	307 (Aug 31)	2.6
	Average year	201 (66)	108 (Feb 18)	300 (Sep 16)	2.8
Ethene ^e	2004			14	
	2006				
	Average year			14	
Ethyne	2004	27 (18)	8 (Jan 7)	58 (Sep 12)	7.6
	2006	35 (23)	7 (Jan 6)	77 (Aug 28)	10.7
	Average year	31 (20)	10 (Mar 12)	71 (Sep 11)	7.2
Propane	2004	20 (13)	5 (Feb 6)	44 (Aug 11)	8.0
	2006	29 (18)	6 (Dec 30)	60 (Aug 12)	10.2
	Average year	24 (15)	7 (Jan 6)	49 (Aug 13)	7.4
<i>n</i> -Butane	2004				
	2006	10 (5)	3 (Dec 12)	18 (Aug 2)	5.5
	Average year	9 (4)	4 (Dec 25)	16 (Jul 26)	4.1
<i>i</i> -Butane ^e	2004				
	2006			12	
	Average year			9.9	
Benzene	1997–98	9 (4)	4 (Feb 5)	17 (Aug 22)	3.8
	2000–01	8 (3)	3 (Feb 11)	13 (Aug 13)	3.9
	Average year	9 (4)	4 (Feb 22)	15 (Aug 17)	3.5

^a Values (in pptv unless noted) are determined from the Fourier series fits.

^b Standard deviation in parenthesis.

^c Date of minimum/maximum in parenthesis.

^d Ratio of the winter maximum to summer minimum.

^e Ethene and *i*-butane were only measured above their LOD (3 pptv) during the winter months. Values listed are the average mixing ratio during the winter.

throughout the summer. This reflects the presence of higher anthropogenic emissions in the northern hemisphere and relatively short transit times to Summit.

At the South Pole, NMHC maxima occurred in late winter or early spring (Table 1 and Fig. 2). During spring ambient hydroxyl concentrations are increasing due to increased photochemical production. As noted above, this results in a decrease in hydrocarbon mixing ratios. The timing of this decrease is dependent on the atmospheric lifetime of the compounds. Compounds that are more reactive with OH are more sensitive to changes in OH concentrations and peak earlier. Hence, *n*-butane has the shortest OH lifetime of the NMHC measured year-round and the earliest maximum based on the Fourier fitting (July 26). Increasing in lifetime, propane and benzene (which have comparable lifetimes) peak on August 13 and 17, respectively, while the fit of ethyne (slightly longer lived) peaks on September 11. The last NMHC to peak (September 16) is ethane which is the longest lived with a lifetime of 1–2 months depending on hydroxyl concentrations. Carbon monoxide has a similar lifetime and peaks on September 21.

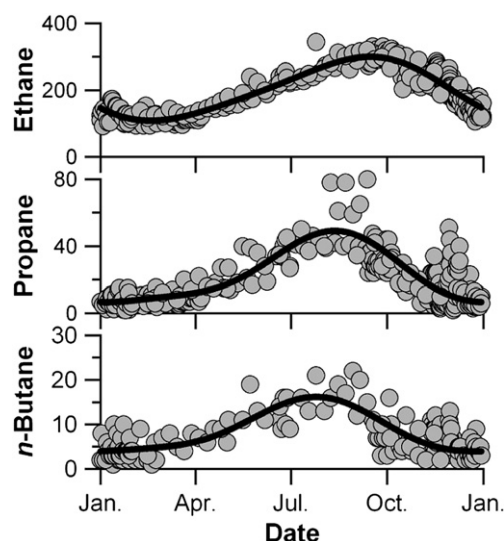


Fig. 2. Select NMHCs (pptv) versus day of year measured at the South Pole during all years. The lines are Fourier fits to the data. The atmospheric lifetime (due to hydroxyl reactivity) is longest for ethane and shortest for *n*-butane.

4.2. Alkyl nitrates

The South Pole average, minimum, and maximum mixing ratios (based on the Fourier series fits) for the five C_1 – C_4 alkyl nitrates measured during 2004 and 2006, along with values for the “average year”, are shown in Table 2. The seasonal cycles for these compounds (Fig. 3) are noticeably different from those for the NMHCs (Fig. 3) in that their maximum mixing ratios occur in early winter (late March–early April). These trends are consistent with those reported in Swanson et al. (2004). However, these earlier observations did not include extensive winter sampling (no samples collected between March 1 and June 1) when the maxima were measured. The most abundant of these species are methyl, ethyl and *i*-propyl nitrate, with peak mixing ratios of 12.8, 3.2 and 2.2 pptv, respectively. Methyl nitrate is found to account for 60–70% (by volume) of the total alkyl nitrates measured, regardless of the time of year.

Table 2

Interannual variation of alkyl nitrates during year-round sampling periods at the South Pole^a.

Compound	Year	Average ^b	Minimum ^c	Maximum ^c
Methyl nitrate	2004	8.4 (2.8)	3.8 (Dec 29)	12.8 (Apr 16)
	2006	8.5 (2.8)	4.1 (Dec 13)	12.8 (Apr 26)
	Average year	8.6 (2.8)	3.7 (Dec 26)	12.8 (Apr 9)
Ethyl nitrate	2004	2.2 (0.7)	0.9 (Jan 7)	3.2 (May 1)
	2006	2.1 (0.7)	1.0 (Dec 15)	3.0 (May 3)
	Average year	2.2 (0.7)	0.9 (Dec 31)	3.2 (Apr 26)
<i>n</i> -Propyl nitrate	2004	0.18 (0.07)	0.09 (Nov 28)	0.28 (Jun 11)
	2006	0.26 (0.09)	0.10 (Dec 16)	0.37 (Apr 26)
	Average year	0.23 (0.08)	0.09 (Dec 17)	0.34 (May 10)
<i>i</i> -Propyl nitrate	2004	1.2 (0.4)	0.5 (Dec 24)	1.8 (Jun 2)
	2006	1.7 (0.7)	0.5 (Dec 26)	2.7 (May 4)
	Average year	1.4 (0.6)	0.4 (Dec 28)	2.2 (May 15)
2-Butyl nitrate	2004	0.36 (0.16)	0.16 (Jan 20)	0.59 (Jul 13)
	2006	0.65 (0.27)	0.17 (Dec 19)	1.02 (Apr 23)
	Average year	0.47 (0.19)	0.15 (Dec 25)	0.71 (May 17)

^a Values (in pptv) are determined from the Fourier series fits.

^b Standard deviation in parenthesis.

^c Date of minimum/maximum for the trend lines in parenthesis.

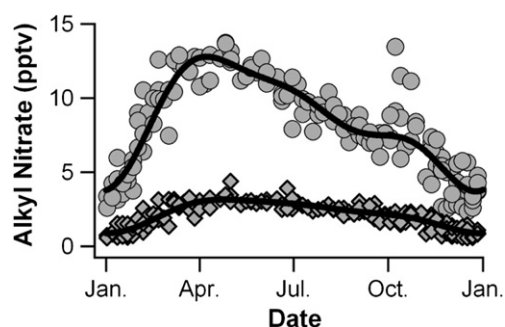


Fig. 3. Methyl (circles) and ethyl nitrate (diamonds) versus day of year measured at the South Pole during all years. The lines are Fourier fits to the data. Propyl and 1-butyl nitrates display similar seasonal cycles.

The alkyl nitrates have a variety of sources, both natural and anthropogenic, depending on the alkyl group. In polluted atmospheres, production is initiated by the reaction between an alkane (RH) and OH (Reaction (1)) followed by the subsequent reaction of the alkyl radical with molecular oxygen (Reaction (2)) to produce a peroxy radical (RO_2). This species can then react with NO to form either an alkyl nitrate ($RONO_2$, Reaction (3)) or an alkoxy radical (RO, Reaction (4)):



The branching ratio between Reactions (3) and (4) is dependent on the alkyl group, with alkyl nitrate production increasing as the number of carbons increases. Thus, this pathway is generally not significant for methyl nitrate and only slightly important for ethyl nitrate but continues to increase in significance as the number of carbons increases. Conversely, atmospheric abundance of the alkanes generally decreases with increasing carbon number. Because of these two factors, propyl- and butyl nitrates are typically the most abundant alkyl nitrates in polluted air masses.

An additional source of short chain alkyl nitrates (C_1 – C_4) was first proposed by Atlas et al. (1993) after observing high concentrations of these compounds in the marine boundary layer. This marine source was later investigated in greater detail by Blake et al. (2003) who determined that the most abundant alkyl nitrate from this source was methyl nitrate with decreasing abundance as the number of carbons in the alkyl nitrate species increased. The exact mechanism by which the alkyl nitrates are formed under marine conditions is still not fully understood, but it is believed that it involves liquid phase reactions between NO and RO_2 (similar to Reaction (3), Dahl et al., 2003) or direct emission by algae (Chuck et al., 2002) and bacteria (Dahl et al., 2007).

The higher mixing ratios of methyl nitrate relative to larger alkyl nitrates observed at the South Pole suggest a strong influence of marine emissions. The C_2 and C_3 alkyl nitrates exhibit good correlation with methyl nitrate and ratios relative to methyl nitrate similar to measurements over the tropical Pacific Ocean (Blake et al., 2003) showing that marine emissions are also the major source of these short-chain alkyl nitrates (Table 3). The correlation of 2-butyl nitrate with methyl nitrate gave a R^2 value of less than 0.4

Table 3

Correlation slopes for alkyl nitrates versus methyl nitrate measured at the South Pole and over the tropical Pacific Ocean^a.

Compound	South Pole		Pacific Ocean ^b	
	2004	2006	1996	1999
Ethyl nitrate	0.21 (0.80)	0.20 (0.67)	0.39 (0.94)	0.34 (0.98)
<i>n</i> -Propyl nitrate	0.017 (0.46)	0.024 (0.52)	0.016 (0.74)	0.020 (0.88)
<i>i</i> -Propyl nitrate	0.11 (0.60)	0.20 (0.51)	0.09 (0.93)	0.11 (0.93)
2-Butyl nitrate	0.029 (0.29)	0.064 (0.37)	0.015 (0.39)	0.018 (0.60)

^a R^2 in parenthesis.

^b From Blake et al. (2003).

suggesting that marine emissions are not its sole source at the South Pole. An additional source of alkyl nitrates from surface snow has been suggested by Swanson et al. (2002). However, this alternate source is not likely the cause of the winter alkyl nitrate maximum because it is photochemical in nature, and thus, absent during the winter.

Following the maxima in early April, the alkyl nitrates systematically decreased until January of the following year (Fig. 3). From April until mid-October (austral winter), this decrease can be seen as 0.030 pptv day⁻¹ for methyl nitrate and 0.043 pptv day⁻¹ for the sum of the alkyl nitrates measured. From mid-October (when polar sunrise occurs) the decreases become more dramatic, leading to minimum mixing ratios in late summer. This alkyl nitrate seasonal pattern is likely the result of at least four factors with overlapping temporal profiles including: (1) seasonal marine emissions; (2) seasonal differences in sea ice extent along the Antarctic coast; (3) seasonally modulated atmospheric removal via OH oxidation; and (4) seasonal differences in transport efficiency of marine air masses (both local and long-range) to the plateau. While oceanic emissions are highest during mid-summer, OH concentrations are also at their highest, thus shifting the seasonal maximum for alkyl nitrates at the South Pole. Transport efficiency, on the other hand, is likely to maximize in early winter. Therefore, it is apparent that to gain a more quantitative understanding of the seasonal trends in the alkyl nitrates and the other biogenically released trace gases in Antarctica, the use of advanced global transport-chemical models is required.

4.3. Other compounds having oceanic sources

Marine emissions are a significant source of methyl iodide and bromoform to the atmosphere (Smythe-Wright et al., 2006; Quack et al., 2007, respectively). However, maximum mixing ratios at the South Pole are observed in mid-winter (June–July) which is beyond the peak in biological activity (Fig. 4). As stated for the alkyl nitrates, this is likely the result of differing temporal trends for production, removal, sea ice extent, and transport efficiency. Large variations can be seen in the annual mixing ratios for these compounds (Table 4) with the highest values being observed in 2004. Bromoform is found to be reasonably well-correlated ($R^2 = 0.71$) with methyl nitrate suggesting similar sources. However, bromoform mixing ratios are nearly constant throughout the winter while methyl nitrate decreases suggesting a more complex interplay of the four factors listed above. In contrast, methyl iodide has a weak correlation with methyl nitrate and bromoform suggesting a differing set of controlling factors (sources and sinks).

The maximum DMS measured at the South Pole was 10 pptv (in April 2006) with typical values at or below the detection limit. In addition, there was no apparent seasonal cycle for DMS (Fig. 5) but the highest DMS mixing ratios were those seen during the fall (April and May) and early summer (November–December). These

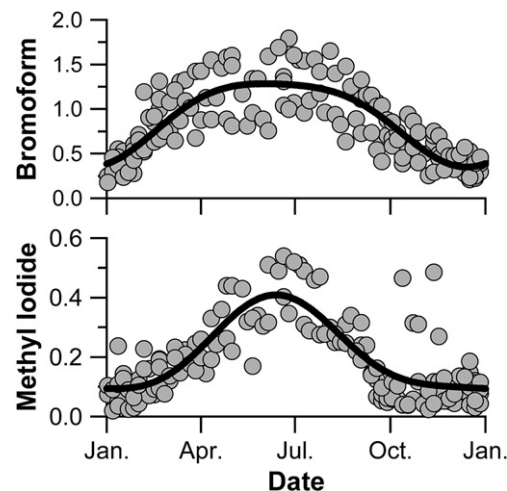


Fig. 4. Seasonal cycle of bromoform and methyl iodide with a Fourier series fit to the data. The spread in the observations is the result of different winter mixing ratios in 2004 and 2006 (Table 4).

same temporal trends appear in measurements of non-sea salt sulfate and methane sulfonate aerosol data collected at the South Pole (D. Davis, paper in preparation).

4.4. Comparison to earlier studies

The majority of the previous VOC measurements in Antarctica have been recorded at coastal sites which are closer to and therefore more easily influenced by anthropogenic and oceanic sources. Table 5 lists seasonal measurements for select NMHC from Antarctic research stations. Alkane values at the South Pole (averages of 201, 24 and 9 pptv for ethane, propane and *n*-butane, respectively) are comparable to the most recent measurements reported at Halley Bay (185, 31 and 5 pptv), a coastal research station at 75°35'S (Read et al., 2007). However, the ethane seasonal cycle at Halley Station differs in the timing of the minimum (early March) and maximum (early September). Thus, the elapsed time from the summer minimum to the winter maximum is significantly shorter at Halley Bay. This is likely due to the shorter amount of total darkness experienced at Halley Bay.

Read et al. (2007) also reported maximum ethene and propene mixing ratios of 157 and 179 pptv in February 2004 at Halley Station which they attributed to oceanic emissions. The lower mixing ratios we observed at South Pole are indicative of efficient removal of these short-lived compounds during transport to the South Pole. At other coastal research stations (Scott Base and Neumayer), seasonal NMHC mixing ratios were typically higher than seen at the South Pole and Halley Station. This might be the result of closer proximity

Table 4

Interannual variation of methyl iodide and bromoform during year-round sampling periods at the South Pole^a.

Compound (pptv)	Year	Average ^b	Minimum ^c	Maximum ^c
Bromoform	2004	1.02 (0.42)	0.31 (Dec 13)	1.47 (Jun 23)
	2006	0.70 (0.22)	0.35 (Dec 7)	0.98 (Jun 15)
	Average year	0.90 (0.34)	0.35 (Dec 15)	1.28 (Jun 3)
Methyl iodide	2004	0.22 (0.16)	0.04 (Nov 3)	0.49 (Jul 3)
	2006	0.19 (0.08)	0.07 (Dec 15)	0.30 (Jun 15)
	Average year	0.22 (0.11)	0.09 (Jan 9)	0.41 (Jun 14)

^a Values (in pptv) are determined from the Fourier series fits.

^b Standard deviation in parenthesis.

^c Date of minimum/maximum in parenthesis.

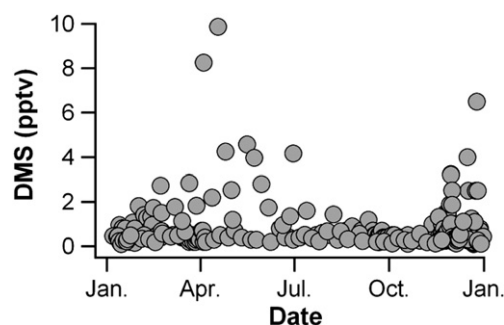


Fig. 5. Dimethyl sulfide measurements versus day of year for all samples.

to anthropogenic sources or significant differences in the calibration standards used at each site.

The only previously reported South Pole NMHC measurements (Khalil and Rasmussen, 1986) found high mixing ratios of ethene (49 ± 6 pptv with no apparent temporal trend) and ethyne (70 pptv) during the summer of 1984. This is in sharp contrast to the current results where ethene was only measured in the austral summer during periods when local pollution was evident and average ethyne mixing ratios were 10 pptv. This discrepancy is most likely the result of local contamination in these earlier published values. This is also suggested by the fact that Khalil and Rasmussen saw no temporal trend in ethene despite increasing photochemical removal during the summer.

Previously, limited measurements of alkyl nitrates have been made in Antarctica (Table 6) with three papers reporting measurements at the German coastal Antarctic station Neumayer. Large variations are seen in these measurements with a minimum methyl nitrate mixing ratio of 9.5 ± 1.4 pptv (during February 1999; Weller et al., 2002) and a maximum of 84 pptv (also during February 1999; Fischer et al., 2002). This variation is likely the result of major shifts in the wind direction during the time that samples were collected at this coastal site. For example, with the wind direction from the open ocean it would be possible to get quite high methyl nitrate levels as reported by Fischer et al. (2002).

Table 5
Comparison of NMHC measurements in Antarctica.

Location		Ethane	Ethyne	Propane	<i>n</i> -Butane
Halley Station ^a	Yearly average	185	19	31	5
	Summer	78		14	
	Winter	293	30	48	10
Neumayer ^b	Yearly average	380	17	84	50
	Summer	292	9	64	40
	Winter	466	28	104	60
Ross Sea ^c	Summer	291	48	61	
Scott Base ^d	Yearly average	288	43		
	Summer	168	20		
	Winter	408	66		
South Pole ^e	Summer	172	70		
South Pole ^f	Yearly average	201	31	24	9
	Summer	108	10	7	4
	Winter	300	71	49	16

Mixing ratios in pptv; seasonal data are averages unless noted.

^a Read et al. (2007); maxima for ethyne and *n*-butane interpolated from graphs.

^b Rudolph et al. (1992).

^c Gros et al. (1998); measurements only made during the summer.

^d Clarkson et al. (1997).

^e Khalil and Rasmussen (1986); measurements from summer 1984.

^f This work; data is from the "average year" Fourier series fits to all samples collected.

Table 6

Average alkyl nitrate mixing ratios during February in Antarctica.

Location	Year	Methyl	Ethyl	<i>n</i> -Propyl	<i>i</i> -Propyl
Neumayer Station	1997 ^a	12	2.7		
	1999 ^b	84	4.6	1.1	0.7
	1999 ^c	9.5 ± 1.4	2.3 ± 0.5	1.1 ± 0.8	1.2 ± 0.5
South Pole ^d	2001–2006	8.9 ± 1.7	1.7 ± 0.6	0.18 ± 0.08	0.9 ± 0.4

^a Jones et al. (1999) with corrections from McIntyre (2001) and Weller et al. (2002).

^b Fischer et al. (2002).

^c Weller et al. (2002).

^d This work; 2001 data previously reported by Swanson et al. (2004).

In contrast, if the wind were coming off of the Antarctic continent, lower mixing ratios would be expected as reported by Weller et al. (2002). The latter are also similar to those measured at the South Pole during February (8.9 ± 1.7 pptv).

The bromoform measurements reported here (ranging from 0.4 to 1.3 pptv) are in relatively good agreement (considering the differences in collection time, location, and calibration standards) with those made during February 1999 at Neumayer Station (0.3 pptv; Fischer et al., 2002) and during November 1989 at McMurdo Sound (0.4–2.0 pptv; Sturges et al., 1993) suggesting limited removal during transport to the South Pole. Likewise, the South Pole seasonal cycle of methyl iodide (0.09–0.41 pptv) is similar to that measured at Syowa Station (0.1–0.6 pptv; Yokouchi et al., 2008). However, these mixing ratios are significantly smaller than the mean methyl iodide mixing ratio of 2.4 pptv estimated from data recorded from October to December on the Antarctic Peninsula by Reifenhäuser and Heumann (1992). The average methyl iodide at the South Pole during this time period was 0.11 pptv giving a coast-to-South Pole ratio of 2.2.

Numerous measurements of DMS with mixing ratios above 100 pptv have been reported in the coastal Antarctic atmosphere and peaking in excess of 1 ppbv at Dumont d'Urville (Preunkert et al., 2007). The DMS seasonal cycle measured at these coastal locations is dependent on oceanic production with peak DMS values occurring during late-summer (January). Conversely, measurements at the Concordia Research Station (Dome C on the Antarctic Plateau and 1100 km inland) showed a significant seasonal cycle peaking in fall and early winter (April–July) at 10 pptv DMS, decreasing throughout the winter, near detection limits in spring and summer, and finally increasing during February (Preunkert et al., 2008). The lower levels of DMS on the plateau (in comparison to coastal sites) are a strong reflection of the very short lifetime of DMS in the marine boundary layer (due to its reaction with BrO and OH) and its relatively short lifetime once on the plateau (approximately 6 h due to average OH concentrations of 2.5×10^6 molecules cm^{-3} as reported by Mauldin et al. (2004)). This combination of highly efficient sinks results in DMS being a very minor sulfur source to the South Pole during the summer months. In fall, longer DMS lifetime (due to reduced levels of OH and BrO) counteract the lower emissions giving a maximum in DMS on the plateau at both Concordia and the South Pole. Interestingly, measurements of methane sulfonate (produced exclusively from the oxidation of DMS) also have shown elevated values in fall and early winter at the South Pole (D. Davis, paper in preparation) and at Concordia (Preunkert et al., 2008).

Although bromoform and methyl iodide may also be considered short-lived species, the lifetime difference between these species and DMS is still quite substantial. For example, using emission rates and burdens for each species the globally averaged lifetime have been estimated at 26 days for bromoform, 7 days for methyl iodide (WMO, 2006), and 1 day for DMS (Kloster et al., 2006). This spread

is the cause for the differences in the seasonal cycles. Bromoform has a very distinct seasonal cycle with similar mixing ratios being observed at the South Pole and the coast. Methyl iodide also was found to have a clear seasonal cycle but South Pole levels differ from those measured on the coast by a about a factor of 2. Meanwhile, DMS which is considerably shorter-lived was found to have no well defined seasonal cycle at the South Pole.

4.5. Comparison to the northern hemisphere (Summit, Greenland)

The annually averaged mixing ratios for VOC measurements at Summit and the South Pole are shown in Table 7. For long-lived species such as methane, OCS and methyl chloride the northern-to-southern hemisphere ratio (NH:SH ratio) is approximately 1, reflecting the efficiency of inter-hemispheric transport for long-lived species. However, for shorter-lived species the NH:SH ratios were higher due to reduced inter-hemispheric transport and greater anthropogenic emissions sources in the northern hemisphere. Thus there is a generally increasing trend in the NH:SH ratio as the lifetime of the species decreases.

The only compound found to have an NH:SH ratio significantly less than one was methyl nitrate (0.30). This likely is due to the fact that the Southern Ocean source for this species is substantially greater than marine areas surrounding Greenland. This source difference is further reflected in the relative abundance of the alkyl nitrates. At the South Pole, methyl nitrate is the most abundant alkyl nitrate while *i*-propyl nitrate is the most abundant at Summit. Lower levels of alkanes in the southern hemisphere also reduce the amount of large alkyl nitrates produced in the atmosphere via Reactions (1)–(4). By contrast, in the northern hemisphere there is an abundance of alkanes resulting in a very high yield of C₂ and larger alkyl nitrates. As shown in Fig. 6, plotting *i*-propyl nitrate (a proxy for photochemically produced alkyl nitrates) versus methyl nitrate (a proxy for oceanic emissions of alkyl nitrates) results in a slope of 0.15 for the South Pole data. This is in good agreement with measurements made by Blake et al. (2003) over the tropical Pacific Ocean, a region dominated by marine production of alkyl nitrates. For Summit, the data give a slope of greater than 3, suggesting that the C₂ and larger alkyl nitrates are primarily

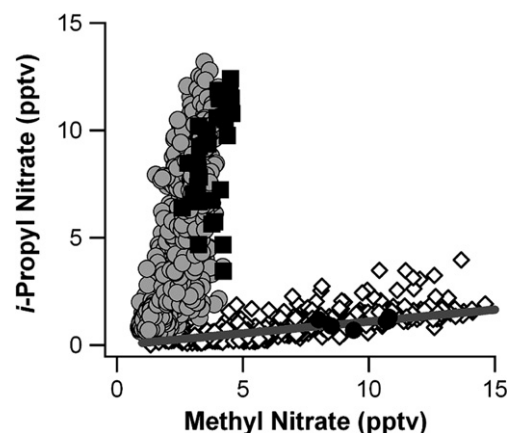


Fig. 6. Scatter plot of *i*-propyl nitrate versus methyl nitrate for all samples collected at the South Pole (diamonds), Summit (gray circles), Neumayer Station (black circles; Weller et al., 2002), and in the Northeast U.S. (squares; Baker, 2008; Baker et al., 2008). The line represents the *i*-propyl nitrate to methyl nitrate ratio measured over the Pacific (Blake et al., 2003).

photochemically produced from their parent alkanes. Measurements by Weller et al. (2002) at Neumayer Station also correlate well with those recorded at South Pole, showing that marine emissions are the primary source of alkyl nitrates throughout the Antarctic region. Also shown in Fig. 6 are measurements made in Boston and New York City (Baker, 2008; Baker et al., 2008) which generally agree well with the slope defined by the Summit data showing photochemical production is the dominant source in both the urban and remote northern hemisphere.

4.6. Aircraft measurements

Major findings and flight details of the ANTICI 2005 airborne study are presented in Slusher et al. (2010). Here we report further detail on the ANTICI VOC measurements which provide the first assessment of the vertical atmospheric structure for several VOCs over the Antarctic continent and illustrate the transport of coastal emissions to the plateau.

As shown in Fig. 7, ethane is nearly constant in the lowest 1.5 km with an average of 210 ± 20 pptv. Above 3 km, ethane increases to 280 ± 20 pptv with the only exception being samples collected while flying through the Mount Erebus plume (discussed below).

Table 7
Annually averaged VOC mixing ratios for Summit and the South Pole.

Compound	Summit ^a	South Pole ^a	NH:SH Ratio ^b	Lifetime (days) ^c
Methane (ppmv)	1.826 (0.012)	1.725 (0.011)	1.06	822
CO (ppbv)	125 (24)	58 (9)	2.14	25
Ethane	1325 (507)	201 (66)	6.58	22
Ethyne	277 (179)	31 (20)	8.80	6.7
Propane	407 (307)	24 (15)	17.17	4.8
Methyl nitrate	2.60 (0.56)	8.62 (2.82)	0.30	229
Ethyl nitrate	2.50 (0.69)	2.23 (0.74)	1.12	29
<i>n</i> -Propyl nitrate	0.76 (0.38)	0.23 (0.08)	3.36	9.1
<i>i</i> -Propyl nitrate	5.74 (3.02)	1.37 (0.59)	4.20	18
2-Butyl nitrate	5.11 (3.59)	0.47 (0.19)	10.97	6.1
OCS	492 (37)	469 (17)	1.05	2630
Methyl chloride	502 (28)	526 (13)	0.95	146
Methyl bromide	9.1 (0.1)	7.0 (0.2)	1.30	181
Methyl iodide	0.30 (0.10)	0.22 (0.11)	1.38	53
Methylene chloride	36 (4)	9 (1)	4.05	53
Methylene bromide	1.1 (0.2)	1.0 (0.1)	1.06	48
Chloroform	11.1 (0.9)	6.2 (0.7)	1.79	50

Mixing ratios in pptv unless noted.

^a Standard deviations in parenthesis.

^b Northern-to-southern hemisphere ratio.

^c Summer lifetimes estimated based on reaction with OH at 298 K and 1 atm (Atkinson, 1997; Atkinson et al., 2006) and a South Pole OH concentration of 2.5×10^6 molecules cm⁻³ (Mauldin et al., 2004).

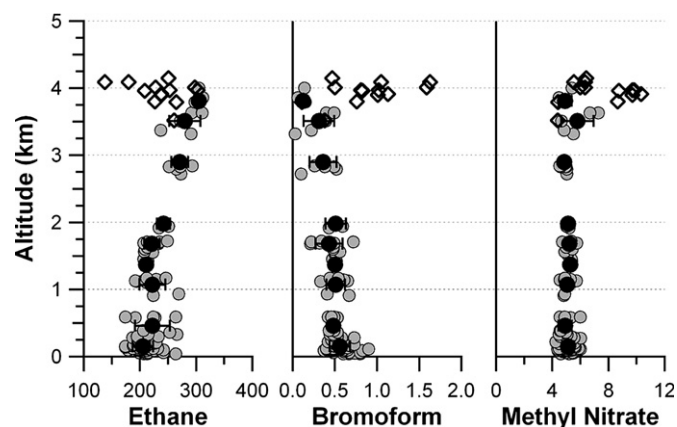


Fig. 7. The vertical structure of ethane, bromoform and methyl nitrate in the coastal Antarctic troposphere. Gray circles represent all data, black circles are altitudinal averages and the diamonds are samples collected in the Mount Erebus plume.

A similar trend was also observed for other NMHCs (Table 8). This trend of increasing mixing ratios with increasing altitude suggests that high altitude long-range transport is the most likely source of NMHCs species in the Antarctic atmosphere. This trend is the opposite of what is typically observed when sampling over populated regions where NMHCs decrease with increasing altitude reflecting strong boundary layer sources (Emmons et al., 2000).

The vertical profiles for bromoform and methyl nitrate are also shown in Fig. 7. Both species show a decreasing trend with increasing altitude due to their strong oceanic sources. However, methyl nitrate has a much weaker altitude trend due to its longer lifetime (methylene bromide and ethyl nitrate also showed similar trends, Table 8). Other compounds (such as DMS and methyl iodide) had no clear trend with altitude. However, increases in all oceanic emitted species were seen while sampling the Mount Erebus plume.

Although one of the goals of ANTICI 2005 was to better characterize DMS distributions in the Antarctic atmosphere, the very low mixing ratios measured on the coast (0.9 ± 1.7 pptv) precluded satisfying this objective. The abnormally low values suggest that there is either low DMS emission during this period, poor vertical mixing, or a combination of factors. The former factor seems likely because the Ross Sea in the vicinity of McMurdo is typically frozen during November and early December. In addition, most sampling was limited to areas 100 km away from open water and at altitudes above 500 m. However, on one occasion (December 10) the aircraft was allowed to fly over open water and measured DMS mixing ratios as high as 11 pptv.

Contrary to the minimal transport of DMS to the South Pole, bromoform was found to be efficiently transported from the coast to the pole (Table 8) with values at the South Pole (0.51 ± 0.09 pptv) comparable to those measured in the lower coastal atmosphere (0.56 ± 0.12 pptv). This is especially noteworthy because of the strong vertical gradient measured for bromoform with values in the upper coastal troposphere of 0.29 ± 0.17 pptv. The transport process by which coastal air masses can reach the plateau is still

poorly understood. However, historical data and results from ANTICI 2005 provide a general picture of these pathways. Hogan (1997) proposed that periodically favorable meteorological conditions develop in the vicinity of the Ross Sea that lead to what he defined as “upslope flow”. During this process coastal air is channeled through the Trans-Antarctic Mountains and reaches the plateau within a few days. Evidence of this phenomenon has been recorded at the South Pole in the form of very abrupt enhancements in temperature, moisture levels and ocean-emitted gases (Swanson et al., 2004). Similarly, Neff (1999) showed that transport of moisture to the South Pole had a well-defined seasonal cycle with transport over West Antarctica and the Ross Sea during spring and fall, while transport was favored from the Weddell Sea during January and February. It was also noted that the March–April time period was one of maximum synoptic weather activity in Antarctica’s coastal areas and at the South Pole. This fall maximum coincides with maximum open water extent in the Southern Ocean providing optimum conditions for transport of oceanically emitted compounds from the coast to the interior of the continent. Unfortunately, there have been no comprehensive studies of the processes in coastal storms that would govern the mixing of compounds with a marine origin into the tropospheric flows that could be transported to the interior of the continent. However, based on an analysis of South Pole back-trajectories associated with high aerosol loadings of non-sea salt sulfate and methane sulfonate, such processes are believed to have a strong seasonal dependence favoring late fall and early winter (D. Davis, paper in preparation).

Although the DMS data from this study falls short in providing the kind of robust data set necessary to demonstrate that one or both of these transport processes occurs, high levels of bromoform at the South Pole suggests that marine boundary layer air does periodically reach the plateau. Bromoform is ideal for illustrating coast-to-plateau transport since its chemical lifetime appears to be longer than that for the transport process itself. DMS, in contrast, has a lifetime shorter than its transport time from the coast to South Pole.

4.7. Mount Erebus plume

A secondary objective of the ANTICI 2005 science plan was to assess the impact of trace gas emissions from Mount Erebus, a continuously active, non-eruptive volcano located on Ross Island within 200 km of McMurdo Station at an elevation of 3.8 km. The plume emitted by the volcano varies in altitude from 3.8 km to 4.2 km, depending on variations in the local wind speed. Direct sampling of the plume was a primary objective of both flights 8 and 9 and a secondary objective of flight 4. Because of the relatively small size of the plume, it was not possible to continuously sample

Table 8

Average VOC mixing ratios in the coastal Antarctic troposphere and at the South Pole.

Compound	Coastal Troposphere		South Pole ^c
	Low altitude ^a	High altitude ^b	
Methane (ppmv)	1.723 (0.008)	1.732 (0.005)	1.727 (0.006)
CO (ppbv)	60 (12)	69 (12)	61 (10)
Ethane	205 (18)	283 (23)	198 (24)
Ethyne	14 (4)	23 (5)	16 (4)
Propane	10 (7)	16 (8)	12 (9)
<i>n</i> -Butane	3.3 (1.4)	7.0 (4.0)	4.2 (1.4)
Benzene	7.1 (2.8)	8.7 (2.4)	5.7 (2.5)
Methyl nitrate	5.12 (0.42)	5.20 (0.82)	5.37 (0.47)
Ethyl nitrate	1.25 (0.34)	1.05 (0.33)	1.24 (0.16)
<i>n</i> -Propyl nitrate	0.14 (0.21)	0.05 (0.02)	0.09 (0.08)
<i>i</i> -Propyl nitrate	0.88 (1.01)	0.61 (0.17)	0.35 (0.20)
2-Butyl nitrate	0.47 (0.71)	0.33 (0.13)	0.07 (0.04)
OCS	487 (22)	491 (12)	471 (22)
DMS	0.86 (1.71)	1.00 (1.26)	0.45 (0.30)
Methyl chloride	542 (12)	557 (13)	537 (20)
Methyl bromide	7.11 (0.69)	7.35 (0.65)	6.71 (0.67)
Methyl iodide	0.17 (0.38)	0.21 (0.34)	0.08 (0.10)
Methylene chloride	8.86 (0.51)	9.41 (0.53)	8.80 (0.58)
Methylene bromide	0.82 (0.05)	0.72 (0.13)	0.81 (0.04)
Chloroform	6.63 (0.38)	6.70 (0.72)	6.32 (0.36)
Bromoform	0.56 (0.12)	0.29 (0.17)	0.51 (0.09)

Mixing ratios in pptv unless noted; standard deviations in parenthesis.

^a Measurements below 1 km.

^b Measurements above 3 km, non-volcanic.

^c Measurements during November and December 2005 (the ANTICI 2005 airborne period).

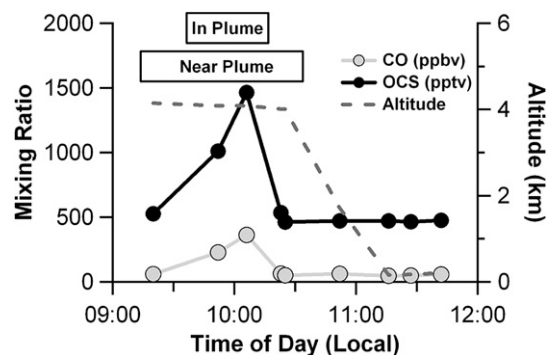


Fig. 8. Carbon monoxide and carbonyl sulfide measured during flight 9 (December 10, 2005).

it while flying. Thus to ensure some significant degree of sampling, porpoising maneuvers were employed.

Of the VOCs measured during these encounters, only OCS and CO consistently increased when the aircraft entered the volcanic plume (Fig. 8). These compounds had exceptionally good correlation in all samples collected near the plume and resulted in a molar ratio for OCS/CO of 3.3×10^{-3} . For comparison purposes, measurements of the emissions in the Mount Erebus crater itself, using an FTIR instrument, resulted in a molar ratio of 3.5×10^{-3} . No other VOCs reported here correlated with either CO or OCS; however, significant correlations were found between SO₂, H₂SO₄, HNO₃, and HO₂NO₂ (Oppenheimer et al., 2009).

As seen in Fig. 7, the volcanic plume samples had decreased levels of ethane and increased levels of halocarbons and alkyl nitrates. At first glance, it appears that the observed shifts could be a result of Erebus volcanic emissions. In an earlier study by Jordan et al. (2000), four different volcanoes were found to emit bromoform and other halocarbons. However, in the present study none of these compounds correlate with the volcanic plume tracers CO and OCS. Instead the observed reductions seen in NMHCs and the elevated halocarbons and methyl nitrate are believed to be the result of upslope flow from the marine boundary layer along the base of Mount Erebus. Thus, the air sampled in and around the volcanic plume appears to be more characteristic of lower elevation coastal atmospheric air.

5. Conclusions

This work further expands on previous VOC measurements in the Antarctic region. As expected, the remoteness of the Antarctic continent, in general, and the South Pole, in particular, limits anthropogenic sources of VOCs. Thus, many of the mixing ratios for VOCs are not only reduced in comparison to urban areas but also to the remote Arctic. The importance of long-range transport was demonstrated based on vertical profiles of anthropogenic VOC species with maximum mixing ratios at the highest altitudes sampled. Conversely, for VOCs associated with marine biogenic emissions, the highest levels were observed at low altitudes.

Measurements of the OCS-to-CO ratio in the Mount Erebus plume were similar to those measured by FTIR within the crater. This reflects the long lifetime for these species relative to the age of the plume even when sampled 60–90 km downwind of the volcano. However, near plume elevated marine generated species such as bromoform and methyl nitrate appear to be a result of upslope flow from the marine boundary layer rather than emissions from the volcano itself.

Further research is needed to understand the South Pole seasonal profiles of several VOCs emitted from the Southern Ocean. Differences seen in the seasonal cycles of these species are believed to reflect the temporal overlap of their sources, sinks and transport to the South Pole. Regional (or possibly global) transport and chemical models are required to gain a quantitative understanding of these cycles. The low levels of DMS measured on the Antarctic plateau at the South Pole and Concordia Station (Preunkert et al., 2008) are in sharp contrast to the numerous observations of elevated DMS at coastal sites. Qualitatively, this result can be understood in terms of the short lifetime of DMS relative to transport times to the plateau.

One of the goals of the ANTCI 2005 campaign was to measure the gradient of DMS between the McMurdo Station and the South Pole. However, no gradient could reliably be measured because DMS levels at both locations averaged below 1 pptv. Because the Antarctic coast near McMurdo is surrounded by sea ice, it is likely that DMS oxidation occurred well before any air mass reached the Ross Sea coastal area. Future studies will need to examine the rapid

oxidation of DMS in a more systematic way than was possible with the constraints placed on the Twin Otter aircraft sampling program in 2005. In addition, measurements later in the summer will allow for determining the gradient during the peak in oceanic production.

Unlike DMS, most species in this work have rarely been measured at coastal Antarctic sites and never over an entire year. Future measurements of these compounds over the source region as well as at the South Pole will allow for improved modeling of the transport and chemical processes controlling their seasonal cycles. As these compounds are produced off the coast of Antarctica and have a long lifetime relative to transport times to the plateau, measurements of their coast-to-South Pole ratio will give insight into the oxidative capacity of the Antarctic atmosphere.

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